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Description

The present invention relates to novel modified alcohols which can be used in the preparation of polymer/polyol dispersions, sometimes termed polymeric polyols or graft polyols and to polymer/polyol dispersions derived from such modified alcohols. The present invention also relates to processes by which such modified alcohols are prepared and to processes which use the polymer/polyol dispersions derived from the modified alcohols. In particular, the present invention relates to novel modified alcohols and their use in the above applications.

The reaction between a polyfunctional isocyanate and a polyfunctional alcohol to produce polyurethane foams, elastomers, resins and the like is a well known chemical reaction which is commercially exploited on a large scale. Commercial polyurethane manufacture in general involves the reaction between a polyfunctional isocyanate and a polyfunctional alcohol such as a polyether polyol. Such polyether polyols are made from a polyfunctional low molecular weight alcohol onto which has been added a polyalkylene oxide chain. The polyalkylene oxide chain is typically prepared as a copolymer of ethylene oxide, propylene oxide or a mixture thereof in a random or block form.

In recent years, the use of polyether polyols of the type described above has been in some areas superseded by polyether polyols containing additional polymeric matter. These polyether polyols, known as polymer/polyols have been described in US 3,304,273, US 3,383,351, US Reissue patent 28,715 and US Reissue patent 29,118. Typically, these polymer/polyols have been prepared by polymerising one or more olefinically unsaturated monomers dispersed in the polyether polyol in the presence of a free radical catalyst. The polymer/polyols produced by these processes, which are thought to comprise a polymer or copolymer of the monomers at least partially grafted to the polyether polyol, have the important advantage of imparting to any polyurethane derived from them improved load-bearing properties as compared with polyether polyols having no additional polymer.

The need to obtain polyurethanes with further improved load-bearing properties has meant that recently attempts have been made to improve polymer/polyols further. In particular developments of polymer/polyols has centred around increasing the polymer content whilst still maintaining the polymer/polyol in the form of a low viscosity fluid having an acceptable resistance to polymer sedimentation and increasing the polystyrene content of the polymer in order to remove problems associated with "scorch".

In order to produce stable low viscosity polymer polyols, it has been proposed to introduce during the polymerisation an extra component often termed a non aqueous dispersant (NAD) stabiliser. The NAD stabiliser comprises a polyol, for example a polyether polyol, containing deliberately added unsaturation which is able to copolymerise with or graft onto the growing polymer chains thereby forming a steric hinderance which prevents the agglomeration of polymer particles.

An example of such an NAD stabiliser is given in US 3,823,201 where there is disclosed an unsaturated polyether polyol obtained by the reaction of a polyether polyol with the anhydride of an unsaturated acid, for example maleic anhydride. In this case, the anhydride of the unsaturated acid reacts with a free hydroxyl group on the polyether polyol to produce a modified polyether polyol having from about 0.10 to 0.70 mole of unsaturation per mole of polyol.

Similar methods of introducing unsaturation into a polyether polyol thereby forming a NAD stabiliser are disclosed in US 4,198,488, GB 1,411,646 and EP 6605.

It has now been found that polymer/polyols having favourable viscosity and resistance to polymer sedimentation at high polymer content can be prepared by polymerising one or more monomers having olefinic unsaturation in a polyether polyol containing a novel NAD stabiliser. The novel NAD stabilisers have the advantage that they are easily prepared in a short time under mild reaction conditions. Such NAD stabilisers also obviate the need for an alkylene oxide capping step as is required when unsaturation is introduced via maleic anhydride.

GB 804,369 and GB 941,291 disclose *inter alia* vinyl silane derivatives.

Accordingly, the present invention provides novel modified alcohols suitable for use as NAD stabilisers as described in Claims 1—4.

The present invention also provides new polymer/polyol dispersions as described in Claims 5—10. The modified alcohols of these dispersions are more generally defined as the reaction product obtained by reacting an alcohol with a silicon atom containing compound having at least one olefinically unsaturated functional group and at least one functional group attached to the silicon atom which is reactable with the hydroxyl groups on the alcohol.

The alcohols used in the preparation of the NAD stabiliser can be for example polyalkylene polyether monoals or polyols, polyhydroxyl containing polyesters, polyhydroxy terminated polyurethane polymers, and polyhydric polythioethers. A preferred class of polyol is the polyalkylene polyether polyols, usually called polyether polyols, of which the following sub-classes are the most preferred

- (a) alkylene oxide adducts of non-reducing sugars and their derivatives.
- (b) alkylene oxide adducts of polyphenols
- (c) alkylene oxide adducts of polyhydroxyalkanes.

The poly ether polyol used should have a number average molecular weight in excess of 400 and a

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hydroxyl number in the range 20 to 280. Terms such as number average molecular weight and hydroxyl number will be familiar to those skilled in the art.

Most preferably the polyether polyol is a poly(ethylene oxide and/or propylene oxide) adduct of one of the following polyhydric alcohols; glycerol, trimethylolpropane, diethylene glycol, the isomeric butanetriols, pentanetriols and hexanetriols and pentaerythritol.

The silicon compound which is used to introduce olefinic unsaturation into the alcohol is a silicon containing compound having at least one olefinically unsaturated functional group and at least one functional group, which is reactable with the hydroxyl groups on the alcohol, attached to the silicon atom or one of the silicon atoms present in the compound if more than one silicon atom is present.

A preferred class of such silicon compounds is that having the generic formula $R_nSi(X)_{4-n}$ where;

(a) n is an integer from 1—3,

(b) the R groups are independently saturated or unsaturated hydrocarbyl groups and where at least one R group is an olefinically unsaturated hydrocarbyl group.

(c) the X groups are independently functional groups which are reactable with the hydroxyl groups on the polyol.

As regards the saturated hydrocarbyl groups, these can be alkyl or cycloalkyl groups or even aryl groups since in general any unsaturation present in such groups will be unreactive. Preferably the saturated hydrocarbyl groups are selected from C_1 — C_{20} linear or branched alkyl groups, cycloalkyl groups having between 4 and 20 carbon atoms in the ring and substituted or unsubstituted phenyl or benzyl groups.

The unsaturated hydrocarbyl groups are ones having olefinic unsaturation and include C_1 — C_{20} alkenyl groups, for example vinyl groups, propenyl groups, butenyl groups and, pentenyl groups, as well as cycloalkenyl groups and olefinically substituted aryl groups. Unsaturated hydrocarbyl groups having more than one unit of olefinic unsaturation e.g. butadienyl groups can also be used.

As mentioned earlier, the X groups are functional groups which are reactable with the hydroxyl groups on the alcohol. Any functional group which can be made to react either directly or indirectly with a hydroxyl group can be used providing that the conditions required to engineer such a reaction are not such that either the polyol or the silicon compound is chemically or thermally degraded. Functional groups capable of reacting with the hydroxyl groups on the polyol include alkoxy groups, preferably C_1 — C_{10} alkoxy groups, halide groups, carbamic acid ester groups of formula $-NHCO_2Z$ where Z is a hydrocarbyl radical and $-OY$ groups where Y is a halogen. Of these X groups, the C_1 — C_{10} alkoxy groups are the most preferred.

Suitable examples of the silicon compounds of the class described above therefore include vinyltrialkoxysilanes e.g. vinyltriethoxysilane, vinyltrimethoxysilane and vinyltripropoxysilane, alkyl vinyl-dialkoxysilanes e.g. methylvinyl diethoxysilane, dialkylvinylalkoxysilanes and, alkyldivinylalkoxysilanes and the like.

In the Examples given above, the carbon carbon double bond, which is the source of the olefinic unsaturation, is bonded directly to the silicon atom. The carbon carbon double bond can, however, also be bonded to the silicon atom through other atoms as in for example the vinylsilane stabiliser methacryloxy-propyl trimethoxysilane.

In addition to the preferred class of silicon atom containing compounds described above, those compounds having the generic formula



can also be used. In the above formula R, X and n are as described previously, p is an integer greater than zero and R^1 is a hydrocarbyl group. An example of such a stabiliser is



The NAD stabiliser produced from the alcohol and the silicon atom containing compound has preferably a viscosity in the range $50-400 \text{ Kg m}^{-1} \text{ s}^{-1}$ at 25°C . In addition the NAD stabiliser should have less than 0.8% by weight, preferably 0.3 to 0.7% by weight induced unsaturation.

In a further aspect of the invention described above there is provided a process for the preparation of the NAD stabiliser by reacting the silicon compound with the polyol. Typically this reaction is carried out by heating the silicon compound and polyol together at temperature in the range 60 to 160°C , preferably 100 to 120°C , optionally in an inert solvent such as cyclohexane or toluene. In the case where the X groups on the silicon compound are alkoxy groups or carbamic acid ester groups, it is preferable to carry out the reaction in the presence of a transesterification or transesterification catalyst for example an acid such as a mixture of trifluoroacetic acid and sodium acetate or a base such as an amidine or guanidine. When an acid catalyst is used it may be necessary to add a neutralising agent, for example sodium bicarbonate, at the end of the reaction.

As mentioned earlier, the NAD stabilisers described above are particularly useful for preparing polymer/polyol dispersions containing high levels of polymer. The fluid polymer/polyol dispersions are prepared by polymerising one or more monomers in a liquid polyol under polymerisation conditions and in

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the presence of a free radical catalyst characterised in that the liquid polyol comprises (1) a base polyol and (2) an NAD stabiliser of the type described above.

The base polyol used in the preparation of the fluid polymer/polyol may be any of the polyols described earlier in relation to the NAD stabiliser or a mixture of such polyols. The base polyols should have viscosities in the range $10\text{--}500\text{ Kg m}^{-1}\text{ s}^{-1}$ at ambient temperature, preferably in the range $10\text{--}200\text{ Kg m}^{-1}\text{ s}^{-1}$.

During the preparation of the polymer/polyol dispersion, a polymer is produced in the liquid base polyol by polymerisation of the monomer or monomers. The monomers used are suitably vinyl monomers, for example, styrene, acrylonitrile, methacrylonitrile and methyl methacrylate. Preferably a mixture of styrene and acrylonitrile are used to produce a copolymer. The final polymer/polyol dispersion is suitably one having more than 20% by weight polymer present and is preferably one having between 30 and 70% by weight polymer. As regards the relative amounts of styrene and acrylonitrile in the copolymer it is desirable for reasons of cost and to reduce scorch to be able to maximise the level of styrene present. Preferably therefore the copolymer should contain between 50 and 100% styrene on a molar basis.

The polymerisation reaction, for example between acrylonitrile and styrene, is initiated by means of a free radical initiator. The free radical initiator can be any of those which are routinely used in vinyl polymerisation processes including peroxides, perborates, persulphates, percarbonates and azo compounds. Typical examples of such free radical initiators include alkyl and aryl hydroperoxides, dialkyl and diaryl peroxides, dialkyl peroxy dicarbonates and azobis(nitriles). Preferred free radical initiators are azobis(isobutyronitrile) and bis(4-tertbutylcyclohexyl)peroxydicarbonate (Perkadox).

The polymer/polyol dispersions produced using the NAD stabilisers of the present invention are useful in the preparation of polyurethanes, particularly polyurethane foams. Such polyurethane foams have improved tensile strength and load bearing without impairment of the other physical parameters associated with the product. Accordingly there is also provided a process for the production of a polyurethane foam by reacting a polyfunctional isocyanate with a polymer/polyol dispersion of the type described above in the presence of

- (a) a catalyst for the urethane forming reaction,
- (b) a blowing agent and
- (c) a foam stabiliser

Polyfunctional isocyanates which can be used to advantage include diisocyanatoalkanes, e.g. 1,2-diisocyanatoethane, 1,3-diisocyanates, the isomeric benzene, xylene and toluene diisocyanates and, MDI.

Catalysts which can be used to accelerate the urethane forming reaction will likewise be familiar to those skilled in the art. These include amines, phosphines, strong inorganic bases, titanate, silicate and stannate esters and organo tin derivatives.

As regards blowing agents and foam stabiliser the range of materials which can be used will be familiar to the skilled man. Thus, suitable blowing agents include water and halogenated hydrocarbons of low molecular weight.

The process may be carried out batchwise or continuously.

The invention is now illustrated by the following examples.

Example 1—Vinyltriethoxy silane derived NAD stabiliser

A two litre reactor containing a mechanical stirrer, fitted with a thermometer, and a Dean Stark apparatus topped by a condenser, was charged with trifluoroacetic acid (2.50 g, 21.9 millimoles), potassium acetate (1.30 g, 13 mmoles), toluene (800 ml), a polyether polyol (1000 g, glycerol started, PO:85%, EO:15%, MW:5000, OH Number: 35.5 mg KOH/g, BP Product Polyurax U10-02) and vinyltriethoxy silane (12.0 g, 75 mmoles). Polyurax is a trade mark.

The reaction mixture was then heated at 110°C during which the transesterification reaction between the polyether polyol and the vinylethoxysilane started producing as products the NAD stabiliser and ethanol. At 110°C a toluene/ethanol azeotrope started to boil and was removed by distillation through the Dean Stark apparatus. By monitoring the levels of ethanol in the distillate using gas chromatography, it was found that the reaction was practically complete after 2 hours. The mixture was then cooled down to 60°C , and neutralized with sodium bicarbonate (2.60 g, 31 mmoles). Toluene was then removed and the product, filtered, had an OH number of 30.6 mg KOH/g, an acid number of 0.78 mg KOH/g., a viscosity of $600\text{ Kg m}^{-1}\text{ s}^{-1}$ at 25°C and an average MW of 12300.

Example 2—Solventless preparation of a NAD stabiliser

A two litre reactor fitted with a mechanical stirrer, a thermometer, a temperature regulating device, a nitrogen supply and a condensor, was charged with a polyether polyol (1000 g, 0.212 mols, glycerol started, PO:85% ED:15%, MW:5000) and degassed for 30 minutes at 100°C under 1 mm HG (1,3 mbar) vacuum. The reactor content was cooled to 60°C and further charged with potassium acetate (0.12 g, 0.0015 mols) and vinyltrimethoxy silane (12.6 g, 0.085 mols).

The mixture temperature was raised to 140°C under 150 ml/minute nitrogen flow for 8 hours. The entrained gases being vented to atmosphere.

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The reactor content was cooled to room temperature, the product polyether polyol was colourless and had a viscosity of $572 \text{ Kg m}^{-1} \text{ s}^{-1}$ at 25°C , a residual unsaturation of 0.15 MEQ per gram.

Example 3—Solventless catalyst free preparation of a NAD stabiliser

A one-litre autoclave fitted with a mechanical stirrer, a thermometer and heat exchanger means was charged with the same polyether polyol (798.2 g, 0.170 mols) as in Example 2 and degassed at .003 bar pressure at 90°C for 30 minutes. The autoclave was then purged with a slight nitrogen flow for 10 minutes charged with vinyltrimethoxy silane (16.62 g, 0.112 mols) and closed in without catalyst addition. The charge was heated at 140°C over 4 hours and then cooled down. The resulting product had the following analysis, viscosity $\text{Kg m}^{-1} \text{ s}^{-1}$ at 20°C : 84. Total unsaturation: (0.186 MEQ/G).

Example 4—Production of modified silicone crosslinker (vinylsiloxane)

A two litre reactor fitted with a mechanical stirrer, a thermometer, a temperature regulating device, and a condensor was charged with vinyltrimethoxysilane (300 g, 2.08 mols), octamethyltetrasiloxane (700 g, 9.46 mols of dimethylsiloxane equivalents) and KOH (0.5 g, 0.0086 mols, 500 ppm). The reactor content was heated to 140°C for 8 hours under slight reflux and cooled without further treatment of the equilibrate. The product had a viscosity at 21°C of 6.6 cps and had the formula



Example 5—Solventless preparations of NAD stabilisers based on the modified silicone crosslinker of Example 4

Two NAD stabilisers were prepared using the procedure described in Example number 2. The charge and analysis were:

Composition properties of products	Sample 1	Sample 2
Polyether polyol Example 2 (g)	1000	1000
Vinylsiloxane from Example 4 (g)	34.98	41.98
Potassium acetate (g)	0.125	0.125
Viscosity ($\text{Kg m}^{-1} \text{ s}^{-1}$ at 20°C)	350	525

Example 6—Solventless preparation of NAD stabilisers based on monols

Two NAD stabilisers were prepared according to the procedure described in Example 2 except that the alcohol was a polyether monol (butanol started, PO:50%, EO:50%, MW:2.800).

Composition	Sample No. 1	Sample No. 2
Polyether monol (2800 MW) (G)	1,000	1,000
Vinyltrimethoxysilane (G)	12.6	14.5
Potassium acetate (G)	0.120	0.120
Product Analysis		
Viscosity ($\text{Kg m}^{-1} \text{ s}^{-1}$ at 25°C)	157	300
Total unsaturation (MEQ/G)	0.09	0.06

Example 7—Solventless preparation of NAD stabilisers based on an unsaturated monol

Two NAD stabilisers were prepared using the procedure described in Example 2 except that the alcohol was an unsaturated polyether monol (allyl alcohol started, PO:60%, EO:40%, MW:4,000).

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Composition	Sample No. 1	Sample No. 2
Unsaturated monol polyether (G)	1,000	1,000
Vinyltrimethoxysilane (G)	12.3	18.5
Potassium acetate (G)	0.12	0.12
Analysis		
Total unsaturation (MEQ/G)	0.20	0.26

Example 8—Solventless preparation of a NAD stabiliser based on vinylmethyldimethoxysilane

Two NAD stabilisers were prepared using the procedure described in Example 2 except that the silicon atom containing compound was vinylmethyldimethoxysilane.

Composition	Sample No. 1	Sample No. 2
Polymer polyol of 5,000 MW (G)	1,000	1,000
Vinylmethyldimethoxysilane (G)	13.7	19.6
Potassium acetate	0.12	0.12
Analysis		
Viscosity (Kg m ⁻¹ s ⁻¹ at 25°C)	290	300
Total unsaturation (MEQ/G)	0.14	0.16

Example 9—Preparation of polymer/polyol

A one litre reactor equipped with a thermometer, stirrer, graduated dropping funnel and heat exchange means, was charged with a blend of a base polyether (210 g, glycerol started, PO:86%, EO:14%, MW:3500, OH Number: 46.0 mg KOH/g, BP Product: Polyurax U10-01) and the NAD stabiliser of Example 1 (26.5 g, 5%). With stirring and under a slight nitrogen flow, the charge was heated to 125°C, and a stream of styrene (141.2 g, 26.6%), acrylonitrile (60.5 g, 12%), and a polymerization initiator (Perkadox P-16 a product sold by Akzo Chimie, 2.65% g, 0.5%), dispersed in the above described base polyether (90.0 g), was continuously added to the charge during a period of two hours. Perkadox is a trade mark. Upon completion of addition, the reaction mixture was maintained at 125°C for 1 hour. The reaction mixture was then stripped of volatiles for two hours at 110°C, under less than 0.013 bars pressure. The stripped reaction product, a white opaque stable dispersion, had a viscosity of 900 Kg m⁻¹ s⁻¹ at 25°C.

Comparative Experiment A—Preparation of polymer/polyol

In a one litre reactor equipped as described above, was charged a base polyether polyol (210 g of the polyether polyol in above example, without any added stabiliser). With stirring and under a slight nitrogen flow, the charge was heated to 125°C, and a stream of styrene (90.65 g, 21%), acrylonitrile (38.85 g, 9%) and a polymerisation initiator (Perkadox P-16, 2.65 g, 0.5%) dispersed in the above described polyether (90.0 g) was continuously added to the charge during two hours period. Before completion of the addition, a completely coagulated mass of polymer was obtained, blocking the stirrer.

Example 10—Batch preparation of a polymer/polyol dispersion, polymer content 23%, styrene: Acrylonitrile=70:30

A two litre reactor equipped with a stirrer, thermometer and heat exchanger, and a graduated dropping funnel, was charged with a base polyether (597 g, 47.78 weight percent, MW:5000).

While stirring under a slight nitrogen flow, the charge was heated to 125°C, and a stream of:

- (a) NAD stabiliser (62.5 g, S.O w/w percent, product from Example No. 2);
- (b) Azo-bis-isobutyronitril (4.4 g, 0.35 w/w percent, e.g. AZDN-LMC from FBC Limited);
- (c) Styrene (201.3 g), 16.11 w/w percent) and acrylonitrile (86.3 g, 6.9 w/w percent), dispersed in the above described base polyether (298 g, 23.85 w/w percent) was continuously added to the charge during a period of 30 minutes.

The term AZDNC-LMC is a trade mark.

Upon completion of addition, the reaction mixture was maintained at 125°C for 30 minutes.

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The resulting polymer/polyol dispersion had the following analysis:

Viscosity at 25°C (unstripped): 280 Kg m⁻¹ s⁻¹
(stripped at 135°C): 300 Kg m⁻¹ s⁻¹

Filtration hindrance:

150 mesh: 100% pass in 15 seconds
700 mesh: 98% in 300 seconds

Example 11—Preparation of polymer/polyol dispersion

A polymer dispersion was prepared using as base polyether a Polyurax Polyol U10-02 (glycerol starter, PO:65%, EO:15%, MW:5000, OH Number: 35.5 mg KOH/g) and as stabiliser the polyol of Example 1 (13.1% on base polyether). Polyurax is a Trade Mark. The polymer polyol dispersion was prepared by a continuous process in which a premix of total weight (50 kg) comprising polyether polyol/styrene/acrylonitrile/catalyst was prepared in a stirred container and then fed by means of a metering pump, to a jacketted continuous stirred tank reactor (CSTR) of capacity (approximately 2 litres) maintained at a reaction temperature of 125°C±5°C, over a period of approximately 8 hours. The reactor fitted with an external cooling loop with heat exchanger and pumped recirculation (capacity approximately 2 litres) to assist in controlling reaction temperature.

The contents from the reactor then passed to a secondary reactor in the form of a jacketted tube (unstirred), capacity approximately 4 litres, the system being maintained at the same temperature and a positive pressure of 0.3 bars by means of a back pressure valve, before being collected in a receiving vessel at atmospheric pressure. Prior to commencing the premixed feed to the stirred reactor, the system was filled with polymer/polyol dispersion containing 20% of total polymer, and already heated to, and maintained at, 125°C.

The resulting polymer dispersion had the following analysis:

Polystyrene (PS) (%):	29.6
Polyacrylonitrile (PAN) (%):	10.8
Total Polymer (%):	40.4
Filtration hindrance:	
150 mesh 100% Pass (s)	13 14 14
700 mesh (%) Pass	17 06 11
RT:	Residence time number
Viscosity	487 Kg m ⁻¹ s ⁻¹ at 25°C

Example 12—All polystyrene polymer dispersion

A one litre reactor equipped as described in Example 2, was charged with a blend of a base polyether (of Example 2, 190 g), and the stabiliser of Example 1 (24.0 g, 5% on base polyether). With stirring and under a slight nitrogen flow, the charge was heated to 125°C, and a stream of styrene (202 g, 42%), and a polymerization initiator (Perkadox P-16, 4.80 g, 1%) dispersed in the above described base polyether (60 g) was continuously added to the charge during two hours period. Upon completion of addition, the reaction mixture was maintained at 125°C for 1 hour. The reaction mixture was then stripped of volatiles for two hours at 110°C, under less than 0.013 bars pressure. The stripped reaction product, a white opaque stable dispersion, had a polymer content of 41% (analysed by centrifugable solids) and a viscosity of 350 Kg m⁻¹ s⁻¹ at 25°C.

Example 13—Continuous preparation of a polymer/polyol dispersion S/AN:70/30, polymer content 23%

A polymer dispersion was made using the same composition as for Example 10, but was polymerised according to a continuous process as described below.

A premix of 5.1 kg comprising a polyether polyol (3,678 g, 71.95%, MW:5000), a NAD stabiliser (255 g, 4.99%, e.g. product from Example 2), acrylonitrile (360 g, 7.04%), styrene (800 g, 15.65% and AIBN (19.25 g, 0.37%) was prepared in a stirred container and then fed by means of a metering pump to a jacketted continuous stirred tank reactor (CSTR) of 0.2 litre capacity, maintained at 125+/-5°C, over a period of approximately 8 hours. The CSTR was fitted with an external heat exchanger. The contents from the reactor were then passed to a secondary reactor formed by an unstirred jacketted tube of 0.4 litre capacity, maintained at 125+/-5°C, and at a positive pressure of 0.3 bars before being collected in a receiving vessel at atmospheric pressure. Prior to commencing the premixed feed to the stirred reactor, the system was filled with polymer polyol dispersion containing 13% of total polymer which had been previously heated to 125°C.

The resulting polymer/polyol dispersion was homogeneous and after 7 residence times had the following analysis:

Viscosity:

224 Kg m⁻¹ s⁻¹ at 25°C

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Filtration hindrance:

150 mesh: 100% pass in 16 seconds

700 mesh: 100% pass in 300 seconds

- 5 Comparative Example B—Batch preparation of a polymer/polyol dispersion without NAD stabiliser
Example 10 was repeated except that the NAD stabiliser was omitted. The same procedure as described in Example No. 10, resulted in a non homogeneous, lumpy reaction mixture.

- Example 14—Preparation of polymer/polyol dispersions from the NAD stabilisers of Example 5
10 Polymer/polyol dispersions were prepared according to the batch or continuous procedures described in Examples 10 and 13 respectively. The resulting polymer polyol dispersions were homogeneous and had the following analyses.

15	NAD stabiliser	Sample 1 of Example 5	Sample 2 of Example 5
	Filtration hindrance after batch polymerisation:		
20	150 mesh	100% pass in 45 seconds	100% pass in 64 seconds
	700 mesh	12% pass in 300 seconds	30% pass in 300 seconds
25	Filtration hindrance after continuous polymerisation		
30	150 mesh	100% pass in 16 seconds	—
	700 mesh	65% pass in 300 seconds	—

- 35 Example 15—Preparation of polymer/polyol dispersions from the NAD stabilisers from Example 6
Polymer/polyol dispersions were prepared according to the batch polymerisation procedure described in Example 10. The resulting polymer/polyol dispersions were homogeneous and had the following analyses:

40	NAD stabiliser	Sample 1 of Example 6	Sample 2 of Example 6
	Filtration hindrance		
45	150 mesh	60% pass in 60 seconds	76% pass in 300 seconds
	Viscosity	254 Kg m ⁻¹ s ⁻¹ at 25°C	

- Example 16—Preparation of polymer/polyol dispersion from the NAD stabilisers from Example 7
50 Polymer polyol dispersions were prepared according to the batch polymerisation procedure described in Example 10. The resulting polymer/polyol dispersions were homogeneous and had the following analyses:

55	NAD stabiliser	Sample 1 of Example 7	Sample 2 Example 7
	Filtration hindrance		
60	150 mesh	100% pass in 300 seconds	45% pass in 300 seconds

- 60 Example 17—Batch preparation of a polymer/polyol dispersion from the NAD stabiliser of Example 3
A polymer/polyol dispersion was made with the same charge and procedure as in Example 10, except that the NAD stabiliser used was the product from Example 3.
The resulting polymer/polyol dispersion was homogeneous and 75% of a sample passed through a
65 150 mesh filter.

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Exempl 18—Preparation of polym r/p lyol dispersions from th NAD stabilisers from Example 8

Polym r/poly l disp rsions wer prepared according to the batch polymerisation procedure d scribed in Example 10. The resulting polymer/polyol dispersions were homogeneous and had the following analysis:

	NAD stabiliser	Sample 1 of Example 8	Sample 2 of Example 8
5			
10	Filtration hindrance 150 mesh	65% pass in 300 seconds	100% pass in 16 seconds
	700 mesh	—	18% pass in 300 seconds

Claims

1. A modified alcohol suitable for use as an NAD stabiliser characterised in that the modified alcohol is the reaction product obtained by reacting a silicon atom containing compound of formula



wherein the R groups are independently selected from C₁ to C₂₀ linear alkyl groups, C₁ to C₂₀ branched alkyl groups, C₄ to C₂₀ cycloalkyl groups, substituted or unsubstituted phenyl or benzyl groups and olefinically unsaturated hydrocarbyl groups, at least one R group being an olefinically unsaturated hydrocarbyl group; X is a C₁ to C₁₀ alkoxy group and n is an integer from 1 to 3, with a polyether polyol having an average molecular weight in excess of 400 and a hydroxyl number in the range 20 to 280.

2. A modified alcohol as claimed in claim 1 characterised in that at least one R group is an olefinically unsaturated group selected from a vinyl, propenyl, butenyl or methacryloxy propyl group.

3. A modified alcohol as claimed in claim 2 characterised in that the silicon atom containing compound is a vinyltriethoxysilane or vinyltrimethoxysilane.

4. A modified alcohol suitable for use as an NAD stabiliser characterised in that the modified alcohol is the reaction product obtained by reacting a silicon atom containing compound of formula



wherein

(a) n is an integer from 1 to 3;

(b) the R groups are independently saturated or unsaturated hydrocarbyl groups and where at least one R group is an olefinically unsaturated hydrocarbyl group;

(c) p is an integer greater than zero;

(d) R¹ is a hydrocarbyl radical, and

(e) the X groups are, independently, functional groups which are reactable with the hydroxyl groups on the alcohol.

with a polyether polyol having an average molecular weight in excess of 400 and a hydroxyl number in the range 20 to 280.

5. A fluid polymer/polyol dispersion prepared by polymerising, in the presence of a free radical catalyst one or more monomers in a liquid polyol under polymerisation conditions characterised in that the liquid polyol comprises:

(a) a base polyol;

(b) a modified alcohol obtained by reacting an alcohol with a silicon atom containing having at least one olefinically unsaturated functional group and at least one functional group attached to the silicon atom which is reactable with the hydroxyl groups on the alcohol.

6. A fluid polymer/polyol dispersion as claimed in claim 5 characterised in that the modified alcohol is a modified alcohol as defined in either claim 1 or claim 4.

7. A fluid polymer/polyol dispersion as claimed in either claim 5 or claims characterised in that the monomers used in the polymerisation reaction are styrene and acrylonitrile.

8. A fluid polymer/polyol dispersion as claimed in claim 7 characterised in that the polymer produced by polymerising the monomers contains 50—100% styrene on a molar basis.

9. A fluid polymer/polyol dispersion as claimed in claim 7 or claim 8 characterised in that the fluid polymer/polyol dispersion contains more than 20% by weight polymer.

10. A fluid polymer/polyol dispersion as claimed in claim 7 or claim 8 characterised in that the fluid polymer/polyol dispersion contains between 30 and 70% by weight polymer.

11. A process for preparing a modified alcohol which comprises reacting a silicon atom containing compound as defined in either claim 1 or claim 4 with a polyether polyol having an average molecular weight in excess of 400 and a hydroxyl number in the range 20 to 280.

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12. A process for preparing polyurethane foam characterised in that the process comprises reacting a polyfunctional isocyanate with a fluid polymer/polyol dispersion as defined in any one of claims 5 to 10 in the presence of a catalyst for the urethane forming reaction a blowing agent and a foam stabiliser.

5 Patentansprüche

1. Modifizierter, zur Anwendung als ein Stabilisator für eine nichtwässrige Polymerdispersion (NAD-Stabilisator) geeigneter Alkohol, dadurch gekennzeichnet, daß der modifizierte Alkohol das Reaktionsprodukt ist, das durch Umsetzen einer ein Siliziumatom enthaltenden Verbindung der Formel

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worin die Gruppen R unabhängig voneinander ausgewählt sind unter C₁ bis C₂₀ linearen Alkylgruppen, C₁ bis C₂₀ verzweigten Alkylgruppen, C₄ bis C₂₀ Cycloalkylgruppen, substituierten oder unsubstituierten Phenyl- oder Benzylgruppen und olefinisch ungesättigten Kohlenwasserstoffgruppen, wobei wenigstens eine Gruppe R eine olefinisch ungesättigte Kohlenwasserstoffgruppe darstellt; X eine C₁ bis C₁₀ Alkoxygruppe bedeutet und n eine ganze Zahl von 1 bis 3 bedeutet, mit einem Polyetherpolyol mit einem durchschnittlichen Molekulargewicht von über 400 und einer Hydroxylzahl im Bereich 20 bis 280 erhalten worden ist.

2. Modifizierter Alkohol nach Anspruch 1, dadurch gekennzeichnet, daß wenigstens eine Gruppe R eine olefinisch ungesättigte Gruppe, ausgewählt unter einer Vinyl-, Propenyl-, Butenyl- oder Methacryloxypropylgruppe ist.

3. Modifizierter Alkohol nach Anspruch 2, dadurch gekennzeichnet, daß die das Siliziumatom enthaltende Verbindung ein Vinyltriethoxysilan oder Vinyltrimethoxysilan ist.

4. Modifizierter, zur Anwendung als ein Stabilisator für eine nichtwässrige Polymerdispersion (NAD-Stabilisator) geeigneter Alkohol, dadurch gekennzeichnet, daß der modifizierte Alkohol das Reaktionsprodukt ist, das durch Umsetzen einer ein Siliziumatom enthaltenden Verbindung der Formel

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worin

(a) n eine ganze Zahl von 1 bis 3 bedeutet;

(b) die Gruppen R unabhängig voneinander gesättigte oder ungesättigte Kohlenwasserstoffgruppen bedeuten und worin wenigstens eine Gruppe R eine olefinisch ungesättigte Kohlenwasserstoffgruppe darstellt;

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(c) p eine ganze Zahl größer als 0 ist;

(d) R¹ einen Kohlenwasserstoffrest darstellt;

(e) die Gruppen X unabhängig voneinander funktionelle Gruppen bedeuten, die mit den Hydroxylgruppen am Alkohol reaktionssfähig sind,

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mit einem Polyetherpolyol mit einem durchschnittlichen Molekulargewicht von über 400 und einer Hydroxylzahl im Bereich 20 bis 280 erhalten worden ist.

5. Fluide Polymer/Polyoldispersion, hergestellt durch Polymerisieren eines oder mehrerer Monomere in einem flüssigen Polyol unter Polymerisationsbedingungen in Anwesenheit eines freiradikalischen Katalysators, dadurch gekennzeichnet, daß das flüssige Polyol

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(a) ein Grundpolyol;

(b) einen modifizierten Alkohol, erhalten durch Umsetzung eines Alkohols mit einer ein Siliziumatom enthaltenden Verbindung, die wenigstens eine olefinisch ungesättigte funktionelle Gruppe und wenigstens eine an das Siliziumatom gebundene funktionelle Gruppe enthält, die mit den Hydroxylgruppen an dem Alkohol reaktionsfähig ist, umfaßt.

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6. Fluide Polymer/Polyoldispersion nach Anspruch 5, dadurch gekennzeichnet, daß der modifizierte Alkohol ein modifizierter Alkohol gemäß Definition in Anspruch 1 oder Anspruch 4 ist.

7. Fluide Polymer/Polyoldispersion nach Anspruch 5 oder 6, dadurch gekennzeichnet, daß die in der Polymerisationsreaktion verwendeten Monomere Styrol und Acrylnitril sind.

8. Fluide Polymer/Polyol-Dispersion nach Anspruch 7, dadurch gekennzeichnet, daß das durch Polymerisieren der Monomeren erhaltene Polymer 50 bis 100% Styrol, auf Mol-Basis bezogen, enthält.

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9. Fluide Polymer/Polyol-Dispersion nach Anspruch 7 oder 8, dadurch gekennzeichnet, daß die fluide Polymer/Polyol-Dispersion mehr als 20 Gew.-% Polymer enthält.

10. Fluide Polymer/Polyol-Dispersion nach Anspruch 7 oder 8, dadurch gekennzeichnet, daß die fluide Polymer/Polyol-Dispersion zwischen 30 und 70 Gew.-% Polymer enthält.

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11. Verfahren zur Herstellung eines modifizierten Alkohols, welches in Umsetzen einer ein Siliziumatom enthaltenden Verbindung, wie in Anspruch 1 oder Anspruch 4 definiert, mit einem Polyetherpolyol mit einem mittleren Molekulargewicht von über 400 und einer Hydroxylzahl im Bereich 20 bis 280 umfaßt.

12. Verfahren zur Herstellung eines Urethanschaumes, dadurch gekennzeichnet, daß das Verfahren ein Umsetzen eines mehrwertigen Isocyanats mit einer fluiden Polymer/Polyol-Dispersion, wie in einem der

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Ansprüche 5 bis 10 definiert, in Anwesenheit eines Katalysators für die Urethanbildungsreaktion, eines Treibmittels und eines Schaumstabilisators umfaßt.

Revendications

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1. Alcool modifié convenant pour servir de stabilisant de type DNA (dispersant non aqueux), caractérisé en ce que l'alcool modifié est le produit de réaction que l'on obtient en faisant réagir un composé contenant un atome de silicium, de formule

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dans laquelle les groupes R sont choisis, indépendamment, parmi des groupes alkyles linéaires en C₁ à C₂₀, des groupes alkyles ramifiés en C₁ à C₂₀, des groupes cycloalkyles en C₄ à C₂₀, des groupes phényles ou benzyles substitués ou non substitués et des groupes hydrocarbyles à insaturation oléfinique, au moins un
15 groupe R étant un groupe hydrocarbyle à insaturation oléfinique; X représente un groupe alcoxy ayant 1 à 10 atomes de carbone et n est un nombre entier valant 1 à 3, avec un polyéther polyol ayant un poids moléculaire moyen excédant 400 et ayant un indice d'hydroxyle compris entre 20 et 280.

2. Alcool modifié, tel que revendiqué à la revendication 1, caractérisé en ce qu'au moins un groupe R est un groupe à insaturation oléfinique, choisi parmi un groupe vinyle, propényle, butényle ou
20 méthacryloxy propyle.

3. Alcool modifié tel que revendiqué à la revendication 2, caractérisé en ce que le composé contenant un atome de silicium est un vinyltriéthoxysilane ou un vinyltriméthoxysilane.

4. Alcool modifié, convenant pour servir de stabilisant du type DNA, caractérisé en ce que l'alcool modifié est le produit de réaction que l'on obtient en faisant réagir un composé contenant au moins un
25 atome de silicium, de formule



dans laquelle

- (a) n est un nombre entier valant 1 à 3,
- 30 (b) les groupes R représentent, indépendamment, des groupes hydrocarbyles, saturés ou insaturés, et au moins un groupe R représente un groupe hydrocarbyle à insaturation oléfinique;
- (c) p est un nombre entier supérieur à 0;
- (d) R¹ représente un radical hydrocarbyle, et
- (e) les groupes X représentent, indépendamment, des groupes fonctionnels pouvant réagir avec les
35 groupes hydroxyles de l'alcool, avec un polyéther polyol ayant un poids moléculaire moyen excédant 400 et ayant un indice d'hydroxyle compris entre 20 et 280.

5. Dispersion fluide de type polymère/polyol, préparée par la polymérisation, en présence d'un catalyseur engendrant des radicaux libres, d'un ou plusieurs monomères dans un polyol liquide, dans des
40 conditions de polymérisation, dispersion caractérisée en ce que le polyol liquide comprend:

- (a) un polyol de base;
- (b) un alcool modifié, obtenu par la réaction d'un alcool avec un composé contenant au moins un atome de silicium et ayant un groupe fonctionnel à insaturation oléfinique et au moins un groupe fonctionnel fixé sur l'atome de silicium et qui peut réagir avec les groupes hydroxyles de l'alcool.

45 6. Dispersion fluide de type polymère/polyol, telle que revendiquée à la revendication 5, caractérisée en ce que l'alcool modifié est un alcool modifié tel que défini dans l'une des revendications 1 ou 4.

7. Dispersion fluide de polymère/polyol telle que revendiquée à la revendication 5 ou 6, caractérisée en ce que les monomères utilisés dans la réaction de polymérisation sont le styrène et l'acrylonitrile.

8. Dispersion fluide de type polymère/polyol telle que revendiquée à la revendication 7, caractérisée en ce que le polymère, produit par la polymérisation des monomères, contient 50 à 100% de styrène sur base
50 molaire.

9. Dispersion fluide du type polymère/polyol, telle que revendiquée à la revendication 7 ou à la revendication 8, caractérisée en ce que la dispersion fluide de type polymère/polyol contient plus de 25% en poids du polymère.

55 10. Dispersion fluide de type polymère/polyol, telle que revendiquée à la revendication 7 ou 8, caractérisée en ce que la dispersion fluide de type polymère/polyol contient entre 30 et 70% en poids de polymère.

11. Procédé pour préparer un alcool modifié, qui comprend la réaction d'un composé contenant au moins un atome de silicium, selon la définition donnée à la revendication 1 ou à la revendication 4, avec un polyéther polyol ayant un poids moléculaire moyen excédant 400 et ayant un indice d'hydroxyle compris entre 20 et 280.
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12. Procédé pour préparer de la mousse de polyuréthane, caractérisé en ce que ce procédé comprend la réaction d'un isocyanate polyfonctionnel avec une dispersion fluide du type polymère/polyol, telle que définie dans l'une quelconque des revendications 5 à 10, en présence d'un catalyseur pour la réaction de formation d'uréthane d'un agent de gonflement et d'un stabilisant de la mousse.
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